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A Facile Preparation of Geometrically Pure Alkenyl, Alkynyl, and Aryl Conjugated *Z*-Alkenes: Stereospecific Synthesis of Bombykol

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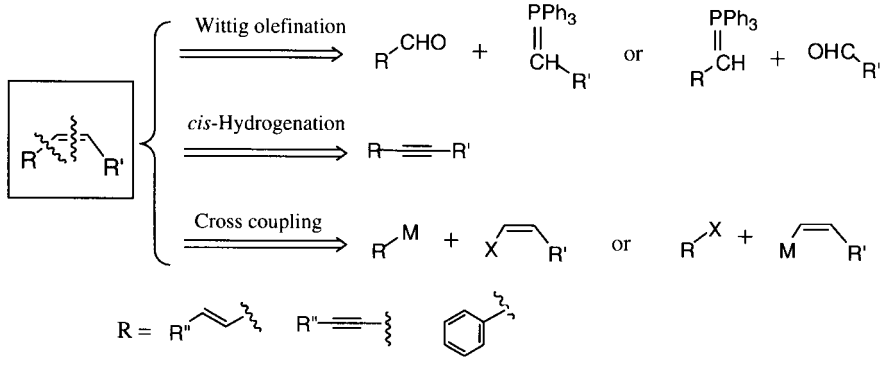
Abstract—Ni- and Pd-catalyzed cross coupling reactions of 2-alkenyl, 2-alkynyl, and 2-aryl substituted (1*Z*)-1-bromoalkene with alkyl Grignard reagents gave 1-alkyl substituted (1*Z*,3*E*)-diene, (1*Z*)-en-3-yne, and (1*Z*)-2-arylethene, each in good yield. When (trimethylsilyl)-methylmagnesium chloride was used as the Grignard reagent, conjugated *Z*-allylsilane was produced. Bombykol, (10*E*,12*Z*)-10,12-hexadecadien-1-ol, a sex pheromone of female moss, *Bombyx mori*, was synthesized stereospecifically.

Stereo- and regio-defined structures of conjugated *E*,*Z*-diene and *E*-enyne have often been observed in a wide variety of natural products.[1] Stereocontrolled preparation of such conjugated *E*,*Z*-diene and *E*-enyne is very important for modern organic synthesis. A number of methodologies for the synthesis of *Z*-alkenyl bonds have been developed; for example, Wittig olefination reaction under kinetic conditions,[2] and *cis* semi-hydrogenation of alkyne.[3] However, for the synthesis of conjugated *E*,*Z*-diene, the major problem for the Wittig-type reaction is how to control selective formation of the desired *E*,*Z*-diene prior to formation of thermodynamically stable *E*,*E*-diene. In fact, preparation of conjugated *Z*-alkene by the Wittig reaction gave a mixture of *E*,*Z*- and *E*,*E*-dienes.[4] *cis* Semi-hydrogenation of *Z*-enyne gave *E*,*Z*-diene stereoselectively but sometimes in low yield due to poor reactivity and chemo-selectivity.[5] A metal-catalyzed cross coupling reaction is the most reliable for preparation of such conjugated alkenes with retention of the configuration[6] (Scheme 1).

We have reported the stereospecific synthesis of *E*,*Z*-diene and *Z*-enyne by the Pd-catalyzed coupling reaction of (1*Z*)-1-bromoalkene with alkenylboronic acid and 1-alkyne, in which the reaction occurred on an sp2 carbon of *Z*-alkenyl bromide with an sp2 and an sp carbon center of alkenyl metal or alkyne.[7] A coupling reaction of (1*Z*)-1-bromo-1,3-diene with an sp3 carbon center could serve as an alternative stereospecific synthesis of such dienes or enynes.[8] In this paper, we report coupling reactions of conjugated 2-alkenyl, 2-alkynyl, and 2-aryl substituted (1*Z*)-1-bromoalkene with alkyl Grignard reagent promoted by a Ni or Pd catalyst, which afforded *E*,*Z*-diene or *Z*-enyne



Scheme 1.

Keywords: cross-coupling; stereospecific reaction; Z-alkene; Z-allylsilane; bombykol.
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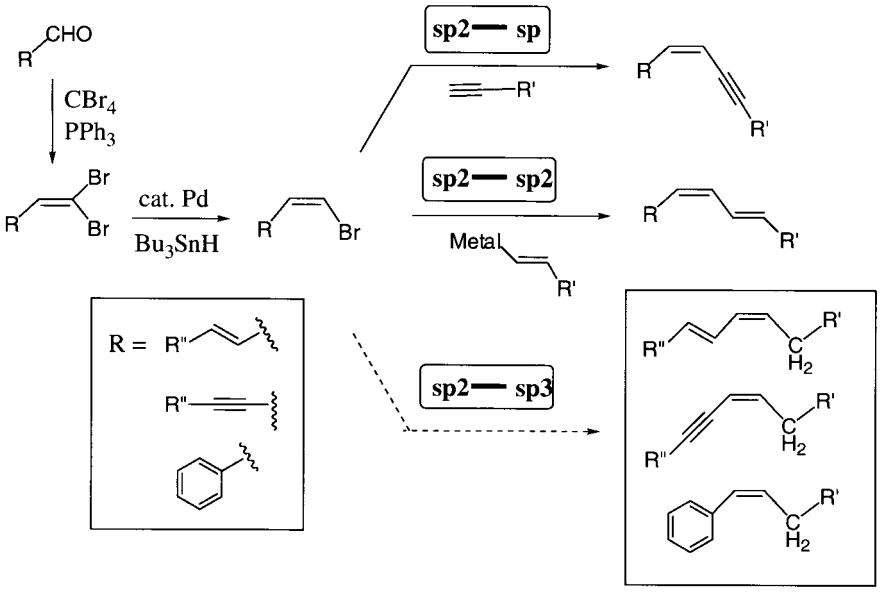
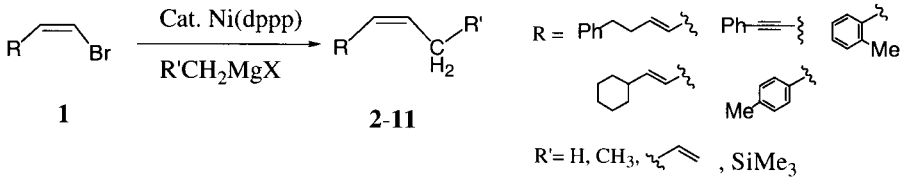


Scheme 2.

and *Z*-β-bromostyrene derivatives stereospecifically (Scheme 2).

The requisite *Z*-bromoalkenes were prepared from the corresponding aldehyde by dibromomethylenation and successive Pd-catalyzed hydrogenolysis with Bu_3SnH by the method reported previously.[7] Bromodiene (**1a**) (R=4-phenylbutenyl) was treated with methylmagnesium bromide in the presence of 4 mol% $NiCl_2$(dppp) at room temperature. The reaction was completed in 1 h to give **2a** (R=4-phenylbutenyl, R′=H) in 78% yield, as shown in Scheme 3. The results, including those of other substrates and reagents, are listed in Table 1. Geometric purity of **1a** was confirmed by its proton NMR spectrum. The coupling constants were identical with 10.8 Hz for *Z*-olefinic and 15.2 Hz for *E*-olefinic bonds, which clearly indicated the structure of *E*,*Z*-diene. The reaction with ethyl, and allylmagnesium bromide with **1a** gave the corresponding alkylated 1,3-dienes, **2b** and **2c**, in 74 and 58% yields, respectively (entries 2 and 3). The reaction of (1*Z*,3*E*)-1-bromo-4-cyclohexyl-1,3-butadiene (**1b**) also gave diene (**3**) in 82% yield (entry 4). (1*Z*)-Bromoalkene conjugated with alkyne **1c** can be alkylated with ethyl and allyl Grignard reagents to give **4a** and **4b** with retention of the configuration in good yields (entries 5 and 6). 2-Alkyl substituted *Z*-styrenes were obtained by the coupling of *Z*-β-bromostyrene with alkyl Grignard reagents. The reactions of (*Z*)-β-bromo-2-methyl and 4-methylstyrenes, **1d** and **1e**, gave ethyl substituted compounds **5** and **6** in each 74% yield, respectively (entries 7 and 8). In all cases, the reactions took place stereospecifically. On the other hand, when (trimethylsilyl)methylmagnesium chloride was used as the Grignard reagent for the coupling of **1a**, conjugated allyltrimethylsilane (**7**) was obtained in 79% yield. Other results for **1b**–**1e** are shown in Table 1. Yields were generally good (entries 9–13), and the stereochemistries have been completely retained. Allyltrimethylsilane is one of the most useful functional groups in organic synthesis.[9] Substituted allylsilanes, (*E*)- and (*Z*)-(alkenylmethyl)trimethylsilanes, have been used as an important building block for stereoselective synthesis.[10] Therefore, the synthesis of geometrically pure (*E*)- or (*Z*)-allylsilanes is of value for stereoselective C–C bond formations.

Since the preparation of 1*Z*-1-bromoalkene from 1,1-dibromoalkene was performed by a Pd catalyst in the presence of Bu_3SnH, and the above coupling reaction also occurred with the same catalyst, these two step reactions could be performed successively in one-pot. Hydrogenolysis of 1,1-dibromo-6-phenyl-1,3-hexadiene with Bu_3SnH in the presence of $Pd(PPh_3)_4$ (4 mol%) afforded (1*Z*,3*E*)-1-bromo-1,3-butadiene (**1a**), to which an excess of Me_3SiCH_2MgCl was added. The reaction proceeded smoothly and gave (*Z*)-allylsilane (**7**) in 73% yield. This process also worked well in the case of alkynyl- and aryl-conjugated 1,1-dibromoalkenes. These results are shown in Table 2. Since the hydrogenolysis of **1** occurred stereoselectively and the cross coupling proceeded with retention of configuration, resulting (*Z*)-allysilanes were obtained in geometrically pure form. $Bu_3SnCH_2SiMe_3$ was a major by-product due to the reaction of Bu_3SnBr and Me_3SiCH_2MgCl, but it was easily separated by silica gel column chromatography. The reaction is operationally



Scheme 3.

Table 1. Ni-catalyzed coupling reaction of conjugated (*Z*)-1-bromoalkenes (**1a–e**) with Grignard reagents ($R'CH_2MgBr$)

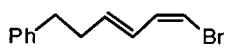
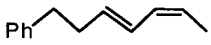
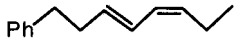
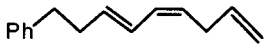
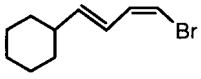
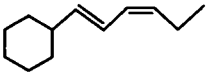
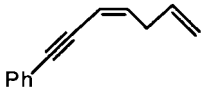
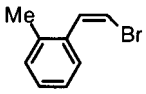
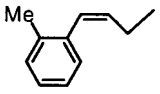
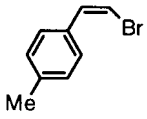
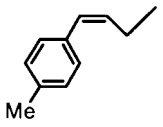
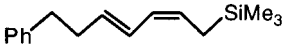
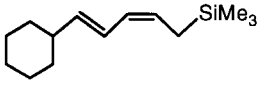
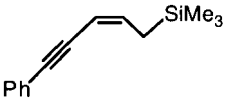
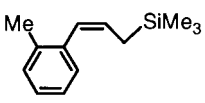
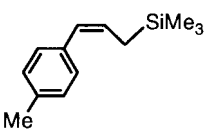
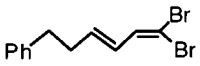
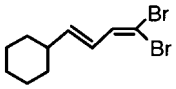
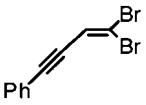
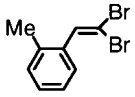
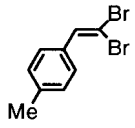
Entry	(*Z*)-Bromoalkene		R'	(*Z*)-Alkene		Yield (%)
1		**1a**	H		**2a**	78
2		**1a**	Me		**2b**	74
3		**1a**	vinyl		**2c**	58
4		**1b**	Me		**3**	82
5		**1c**	Me		**4a**	85
6		**1c**	vinyl		**4b**	83
7		**1d**	Me		**5**	74
8		**1e**	Me		**6**	74
9		**1a**	$SiMe_3$		**7**	79
10		**1b**	$SiMe_3$		**8**	74
11		**1c**	$SiMe_3$		**9**	73
12		**1d**	$SiMe_3$		**10**	67
13		**1e**	$SiMe_3$		**11**	73

Table 2. Pd catalyzed one-pot synthesis of (*Z*)-allylsilanes from 1,1-dibromoalkenes

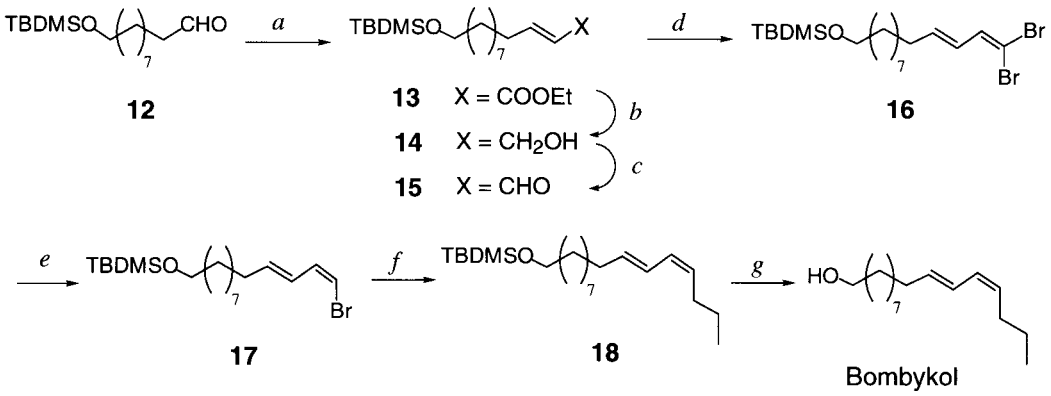
Entry	Dibromoalkene	$ClMgCH_2SiMe_3$ (eq)	(*Z*)-Allylsilane[a]	Yield (%)[b]
1		4	**7**	73
2		5	**8**	77
3		5	**9**	73
4		6	**10**	77
5		6	**11**	73

[a] Geometric purities were determined to be greater than 98% by ^{1}H NMR.
[b] Isolated yield.

simple, and the yield is generally better than that obtained by the stepwise reaction process.

Synthesis of Bombykol

Bombykol is a component of the female sex pheromone of *Bombix mori,* and it was identified and synthesized by Butenant et al. in 1959.[11] It is famous as the first isolated insect sex pheromone. The specific structure, which possesses a consecutive *E,Z*-diene unit on C-16 carbon chain alcohol, has attracted the interest of many synthetic chemists. In fact, a number of the syntheses have been reported so far.[11–16] The most important part of this synthesis is the stereoselective preparation of the *E,Z*-diene moiety. Partial reduction of *E*-enynes,[12] Wittig reaction of enal and ylide or aldehyde and unsaturated ylide,[13] cross coupling reaction of alkenyl metal and haloalkene,[14] isomerization of allene,[15] and others[16] have been reported. Since a lack of facile methods to prepare 1*Z*,3*E*-1-halodiene, construction of *Z,E*-diene from 1*Z*,3*E*-1-halodiene by Kumada–Tamao–Corriu coupling has not been attempted. We have succeeded in the synthesis of geometrically pure bombykol by this strategy. The synthesis is described in Scheme 4. For the introduction of a propyl group, 1*Z*,3*E*-1-bromodiene (**17**) is required. This can be derived from dibromodiene (**16**) by the stereoselective hydrogenolysis. Compound **16** will be easily led from α,β-unsaturatedaldehyde (**15**). This aldehyde can be prepared from aldehyde (**12**) by the standard method. Therefore, the known aldehyde (**12**)[17] is the starting material



Scheme 4. *Reagents and conditions*; *a*, $(EtO)_2POCH_2COOEt$, NaH, THF; *b*, DIBAL, CH_2Cl_2; *c*, Swern oxi.; *d*, CBr_4, Ph_3P, Benzene, *e*, Bu_3SnH, cat. $Pd(PPh_3)_4$; *f*, PrMgCl, cat. Ni(dppp), Et_2O; *g*, Bu_4NF, THF.

of this synthesis. Wittig–Horner–Emmons reaction of **12** with triethyl phosphonoacetate gave α,β-unsaturated ester (**13**) in 83% yield. Reduction of the ester with DIBAL-H to alcohol followed by oxidation under Swern conditions gave α,β-unsaturated aldehyde (**15**) in 67% yield in two steps. Dibromomethylenation with carbon tetrabromide and triphenylphosphine in dichloromethane gave dibromodiene (**16**) in 88% yield. Stereoselective hydrogenolysis with Bu_3SnH in the presence of a Pd catalyst afforded the desired *Z*,*E*-bromodiene (**17**) exclusively in 85% yield. Cross coupling reaction of **17** was performed in the presence of $NiCl_2$(dppp) with propylmagnesium chloride in THF for 22 h at room temperature to give **18** in 84% yield.[18] The geometrical purity of **18** was confirmed to be greater than 98% by ^{1}H NMR spectrum. Finally, deprotection of the TBDMS with Bu_4NF in THF gave bombykol in 93% yield. All of the spectroscopic data of our synthetic sample reported in the literature.

In summary, we have described the synthetic utility of the Ni- and Pd-catalyzed coupling of 1*Z*,3*E*-1-bromo-1,3-dienes with Grignard reagents. The results will be useful not only for the preparation of stereo-defined conjugated *Z*-alkenes but also for the synthesis of polyene natural products bearing a *Z*-alkenyl unit, including insect pheromones.

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded on JEOL LA500 and Varian Gemini 300 for ^{1}H (500 or 300 MHz) and for ^{13}C (125 or 75 MHz). The chemical shifts were shown as δ-values using tetramethylsilane (0 ppm) for proton spectra and $CHCl_3$ (77.0 ppm) for carbon spectra as an internal standard. Infrared spectra (IR) were recorded by the use of a JASCO FT/IR 230 spectrometer and were taken as liquid films on NaCl plates or as tablets. Low and high resolution mass spectra (LRMS and HRMS) were obtained on a JMS MS700 spectrometer at the Analytical Center of Okayama University of Science by the electron impact (EI) method at 70 eV unless otherwise stated. Only significant peaks are described here for IR and MS spectra. Silica gel (Merck 7734, 70–300 mesh) was used for gravity column chromatography and silica gel (Merck 9385, 230–400 mesh) for flash column chromatography. Precoated silica gel plates (Merck 5715, 60F254) were used for thin layer chromatography. All air sensitive reactions were conducted in flame-dried glass ware under an Ar atmosphere. THF and ether were dried over sodium benzophenone ketyl, and methylene chloride was dried over phosphorus pentoxide. These solvents were freshly distilled before use.

General coupling conditions

To a mixture of bromoalkene (1 mmol) and $NiCl_2$(dppp) (4 mol%) in ether (5 mL) was added Grignard reagent (ca 2 mmol) in THF or ether at 0°C. If it needed, the reaction allow to warm up to room temperature. After the reaction completed, the mixture was diluted with hexane, washed with water and brine, and dried over $MgSO_4$. The solvent was removed and the residual oil was purified by column chromatography on silica gel.

(2*Z*,4*E*)-7-Phenyl-2,4-heptadiene (2a). Oil, R_f=0.50 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.73 (3H, dd, *J*=7.1 and 1.7 Hz), 2.43 (2H, dt, *J*=7.2 and 7.3 Hz), 2.72 (2H, t, *J*=7.3 Hz), 5.40 (1H, dq, *J*=10.8 and 7.1 Hz), 5.70 (1H, dt, *J*=15.2 and 7.1 Hz), 5.97 (1H, ddd, *J*=11.0, 10.8 and 1.7 Hz), 6.37 (1H, ddd, *J*=15.2, 11.0 and 1.0 Hz), 7.16–7.32 (5H, m), ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.3, 34.7, 35.9, 124.5, 125.8 (2C), 125.9, 128.3, 128.4 (2C), 129.3, 133.2, 141.9: MS (EI) *m*/*z* (relative intensity) 172 (M^+, base), 156 (16), 143 (32), 141 (30), 115 (55), 99 (23), 98 (21), 97 (21). HRMS (EI) Calcd for $C_{13}H_{16}$: M^+, 172.1252. Found: *m*/*z* 172.1246.

(3*E*,5*Z*)-1-Phenyl-3,5-octadiene (2b). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (3H, t, *J*=7.5 Hz), 2.17 (2H, double quintet, *J*=1.5 and 7.5 Hz), 2.42 (2H, dt, *J*=7.3 and 7.4 Hz), 2.71 (2H, t, *J*=7.4 Hz), 5.32 (1H, dt, *J*=10.7 and 7.5 Hz), 5.70 (1H, dt, *J*=15.0 and 7.3 Hz), 5.91 (1H, dd, *J*=10.9 and 10.7 Hz), 6.34 (1H, ddd, *J*=15.0, 10.9 and 1.5 Hz), 7.19–7.30 (5H, m), ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 21.0, 34.7, 35.8, 125.8, 126.1 (2C), 127.8, 128.3, 128.4 (2C), 132.2, 133.3, 141.8: MS (EI) *m*/*z* (relative intensity) 186 (M^+, base), 143 (9), 130 (17), 115 (14), 95 (83), 91 (36), 67 (14). HRMS (EI) Calcd for $C_{14}H_{18}$: M^+, 186.1409. Found: *m*/*z* 186.1417.

(4*Z*,6*E*)-9-Phenyl-1,4,6-nonatriene (2c). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (2H, dt, *J*=7.3 and 7.2 Hz), 2.72 (2H, t, *J*=7.2 Hz), 2.91 (2H, ddd, *J*=7.2, 6.9 and 1.5 Hz), 4.99 (1H, ddt, *J*=10.2, 1.7 and 1.5 Hz), 5.05 (1H, ddt, *J*=17.1, 1.7 and 1.5 Hz), 5.34 (1H, dt, *J*=10.8 and 7.2 Hz), 5.74 (1H, dt, *J*=15.0 and 7.3 Hz), 5.82 (1H, ddt, *J*=17.1, 10.2 and 6.9 Hz), 6.02 (1H, dd, *J*=10.9 and 10.8 Hz), 6.33 (1H, ddd, *J*=15.0, 10.9 and 1.1 Hz), 7.18–7.31 (5H, m), ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.9, 34.7, 35.8, 114.9, 125.8, 125.9 (2C), 126.9, 128.3, 128.4 (2C), 129.5, 134.2, 136.6, 141.8: MS (EI) *m*/*z* (relative intensity) 198 (M^+, 4), 167 (7), 131 (11), 115 (8), 107 (14), 91 (base), 79 (65), 77 (24), 65 (22). HRMS (EI) Calcd for $C_{15}H_{18}$: M^+, 198.1409. Found: *m*/*z* 198.1434.

(1*E*,3*Z*)-1-Cyclohexyl-1,3-hexadiene (3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (3H, t, *J*=7.6 Hz),1.08–1.30 (6H, m), 1.62–1.75 (4H, m), 1.96–2.12 (1H, m), 2.18 (2H, qdd, *J*=7.6, 7.6 and 1.5 Hz), 5.30 (1H, dt, *J*=11.0 and 7.6 Hz), 5.61 (1H, dd, *J*=15.2 and 7.1 Hz),5.91 (1H, dd, *J*=11.1 and 11.0 Hz), 6.27 (1H, ddd, *J*=15.2, 11.1 and 1.5 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 21.0, 26.0 (2C), 26.2 (2C), 32.9, 41.0, 122.9, 128.3, 131.8, 140.5: MS (EI) *m*/*z* (relative intensity) 164 (M^+, base), 135 (79), 121 (34). HRMS (EI) Calcd for $C_{12}H_{20}$: M^+, 164.1565. Found: *m*/*z* 164.1575.

(*Z*)-1-Phenyl-3-hexen-1-yne (4a). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (3H, t, *J*=7.5 Hz), 2.34 (2H, dq, *J*=7.3 and 7.5 Hz), 5.57 (1H, d, *J*=10.6 Hz), 5.90 (1H, dt, *J*=10.6 and 7.3 Hz), 7.22–7.38 (5H, m), ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 23.8, 86.3, 93.4, 108.3, 123.6, 128.0, 128.3, 131.4, 145.8: MS (EI) *m*/*z* (relative intensity) 156 (M^+, base), 155 (53), 141 (97), 128 (29), 115 (78), 91 (24). HRMS

(EI) Calcd for $C_{12}H_{12}$: M^+, 156.0939. Found: *m/z* 156.0962.

(*Z*)-7-Phenyl-1,4-heptadien-6-yne (4b). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.16 (2H, ddm, *J*=7.3 and 6.9 Hz), 5.06 (1H, dm, *J*=10.1 Hz), 5.13 (1H, dm, *J*=17.1 Hz), 5.74 (1H, dm, *J*=10.7 Hz), 5.88 (1H, ddt, *J*=17.1, 10.1 and 6.9 Hz), 5.99 (1H, dt, *J*=10.7 and 7.3 Hz), 7.30–7.74 (5H, m), ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.6, 86.0, 94.0, 110.0, 115.7, 123.5, 128.1, 128.3, 131.4, 135.5, 140.8: MS (EI) *m/z* (relative intensity) 168 (M^+, 41), 167 (base), 165 (46), 153 (35), 152 (57). HRMS (EI) Calcd for $C_{13}H_{12}$: M^+, 168.0939. Found: *m/z* 168.0977.

(*Z*)-2-(1-Butenyl)toluene (5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (3H, t, *J*=7.4 Hz), 2.16 (2H, dq, *J*=7.4 and 7.3 Hz), 2.27 (3H, s), 5.07 (1H, dt, *J*=11.4 and 7.3 Hz), 6.39 (1H, d, *J*=11.4 Hz), 7.12–7.19 (4H, m), ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.4, 19.9, 21.7, 125.2, 126.7, 127.2, 129.0, 129.7, 134.4, 136.2, 136.8: MS (EI) *m/z* (relative intensity) 146 (M^+, 53), 131 (base). HRMS (EI) Calcd for $C_{11}H_{14}$: M^+, 146.1096. Found: *m/z* 146.1081.

(*Z*)-4-(1-Butenyl)toluene (6). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (3H, t, *J*=7.4 Hz), 2.18 (3H, s), 2.19 (2H, qd, *J*=7.4 and 1.8 Hz), 5.45 (1H, dt, *J*=11.6 and 7.4 Hz), 6.20 (1H, d, *J*=11.6 Hz), 6.97 (2H, d, *J*=8.2 Hz), 7.02 (2H, d, *J*=8.2 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 21.1, 22.0, 128.1, 128.6 (2C), 128.8 (2C), 134.0, 134.9, 136.0: MS (EI) *m/z* (relative intensity) 146 (M^+, base), 131 (100). HRMS (EI) Calcd for $C_{11}H_{14}$: M^+, 146.1096. Found: *m/z* 146.1073.

Synthesis of allylsilane

(Trimethylsilyl)methylmagnesium chloride (1 M solution in ether) was used as the Grignard reagent under the above conditions.

(2*Z*,4*E*)-7-Phenyl-1-trimethylsilyl-3,5-heptadiene (7). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (9H, s), 1.61 (2H, d, *J*=9.2 Hz), 2.41 (2H, dt, *J*=7.5 and 7.3 Hz), 2.70 (2H, t, *J*=7.5 Hz), 5.36 (1H, dt, *J*=10.1 and 9.2 Hz), 5.64 (1H, dt, *J*=14.7 and 7.3 Hz), 5.88 (1H, dd, *J*=10.8 and 10.1 Hz), 6.27 (1H, ddt, *J*=14.7, 10.8 and 1.2 Hz), 7.14–7.29 (5H, m), ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.8 (3C), 19.4, 34.7, 36.0, 125.8, 126.3, 126.4 (2C), 126.7, 128.3, 128.4 (2C), 131.9, 141.9: MS (EI) *m/z* (relative intensity) 244 (M^+, 5), 153 (15), 91 (7), 72 (base). HRMS (EI) Calcd for $C_{16}H_{24}Si$: M^+, 224.1647. Found: *m/z* 224.1664.

(1*E*,3*Z*)-1-Cyclohexyl-5-trimethylsilyl-1,3-hexadiene (8). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.01 (9H, s), 1.00–1.38 (6H, m),1.62 (2H, dd, *J*=8.9 and 1.3 Hz), 1.67–1.99 (4H, m), 1.94–2.08 (1H, m), 5.36 (1H, dt, *J*=10.4 and 8.9 Hz), 5.57 (1H, dd, *J*=15.2 and 6.8 Hz), 5.88 (1H, dd, *J*=10.8 and 10.4 Hz), 6.21 (1H, ddt, *J*=15.2, 10.8 and 1.3 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.7 (3C), 19.3, 26.1 (2C), 28.2 (2C), 33.1, 40.9, 123.2, 126.3, 126.7, 139.0: MS (EI) *m/z* (relative intensity) 222 (M^+, 16), 148 (22), 73 (base). HRMS (EI) Calcd for $C_{14}H_{26}Si$: M^+, 222.1804. Found: *m/z* 222.1770.

(*Z*)-1-Phenyl-5-trimethylsilyl-3-penten-1-yne (9). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.09 (9H, s), 1.94 (2H, d, *J*=8.8 Hz), 5.57 (1H, d, *J*=10.2 Hz), 6.06 (1H, dt, *J*=10.2 and 8.8 Hz), 7.28–7.44 (5H, m), ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.5, 23.1, 87.3, 93.3, 106.1, 124.1, 127.7, 128.3 (3C), 131.3 (3C), 141.5: MS (EI) *m/z* (relative intensity) 214 (M^+, 21), 199 (21), 73 (base). HRMS (EI) Calcd for $C_{14}H_{18}Si$: M^+, 214.1178. Found: *m/z* 214.1184.

(*Z*)-2-[3-(Trimethylsilyl)propenyl]toluene (10). Oil, R_f= 0.71 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.02 (9H, s), 1.64 (2H, d, *J*=8.7 Hz), 2.25 (3H, s), 5.76 (1H, dt, *J*=11.4 and 8.7 Hz), 6.32 (1H, d, *J*=11.4 Hz), 7.12–7.23 (4H, m), ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.7 (3C), 19.1, 19.9, 125.2, 126.1, 126.4, 128.6, 129.0, 129.8, 136.2, 137.1: MS (EI) *m/z* (relative intensity) 204 (M^+, base), 189 (21), 115 (13), 74 (15), 73 (100). HRMS (EI) Calcd for $C_{13}H_{20}Si$: M^+, 204.1334. Found: *m/z* 204.1340.

(*Z*)-4-[3-(Trimethylsilyl)propenyl]toluene (11). Oil, R_f= 0.68 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (9H, s), 1.82 (2H, dd, *J*=9.1 and 1.5 Hz), 2.34 (3H, s), 5.66 (1H, dt, *J*=11.6 and 9.1 Hz), 6.29 (1H, d, *J*=11.6 Hz), 7.15 (2H, d, *J*=8.1 Hz), 7.23 (2H, d, *J*=8.1 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.6 (3C), 19.6, 21.1, 126.7, 128.2, 128.5 (2C), 128.8 (2C), 135.3, 135.6: MS (EI) *m/z* (relative intensity) 204 (M^+, 89), 189 (19), 74(24), 73 (base). HRMS (EI) Calcd for $C_{13}H_{20}Si$: M^+, 204.1334. Found: *m/z* 204.1353.

One pot synthesis of allylsilanes, 7–11 from dibromodiene

To a THF solution of Pd catalyst, prepared from $Pd(OAc)_2$ (4 mol%) and Ph_3P (16 mol%) in THF (5 mL) with stirring for 15 min at room temperature, were added 1,1-dibromo-1,3-diene (1 mmol) in THF (5 mL) and Bu_3SnH (1.1–1.2 mmol). After the hydrogenolysis was completed, an excess of Me_3SiCH_2MgCl (4–6 mmol, 1M in Et_2O) was added and the mixture was stirred for 1–6 h. The standard work up and purification by silica gel chromatography gave **7–11**.

Synthesis of bombykol

Ethyl (*E*)-12-(*tert*-butyldimethylsilyl)oxy-2-dodecenoate (13). To a suspension of NaH (1.54 mmol, 62 mg, 60% in mineral oil) in THF (1.5 mL) was added triethyl phosphonoacetate (0.31 mL, 1.54 mmol) slowly on an ice bath. After the mixture became clear, 10-(*tert*-butyldimethylsilyl)oxydecanal (**12**) (400 mg, 1.4 mmol) in THF (1 mL) was dropped at room temperature. After the reaction mixture was stirred for 1 h, ice water (10 mL) was added and the mixture was extracted with 20% EtOAc in hexane (60 mL). The extract was washed with water and brine, and dried over $MgSO_4$. The solvent was removed and the residual oil was purified by column chromatography on silica gel eluted with 5% EtOAc in hexane to give **13** (417 mg) in 83% yield. Oil, R_f=0.39 (5% EtOAc in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (6H, s), 0.89 (9H, s), 1.28 (3H, t, *J*=7.1 Hz), 1.28 (10H,m), 1.39–1.52 (4H, m), 2.19 (2H, tdd, *J*=6.0, 6.0, and 1.6 Hz), 3.59 (2H, t, *J*=6.6 Hz), 4.19 (2H, q, *J*=7.1 Hz), 5.81 (1H, dt, *J*=15.6 and 1.6 Hz), 6.95

(1H, td, J=15.6 and 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.4, 14.2, 18.3, 25.7, 25.9, 27.9, 29.0, 29.2, 29.3, 29.4, 32.1, 32.8, 60.0, 63.2, 121.1, 149.3, 166.6; IR (neat) 1720, 1650 cm^{-1}; MS (FAB) m/z 357 (MH^+, base). HRMS Calcd for $C_{20}H_{41}O_3Si$: MH^+, 357.2825. Found: m/z 357.2829.

(*E*)-12-(*tert*-Butyldimethylsilyl)oxy-2-dodecen-1-ol (14). To a stirred solution of **13** (772 mg, 2.16 mmol) in anhydrous CH_2Cl_2 (10 mL) was dropped DIBAL-H (4.28 mmol, 4.5 mL in 0.95 M hexane solution) at −78°C. After the mixture was stirred for 30 min at the same temperature, sat. NH_4Cl (30 mL) was added and stirred for 15 min. The formed precipitate was filtered through a Celite pad under vacuum. The filtrate was extracted with EtOAc (130 mL) and washed with water and brine. After drying over $MgSO_4$, the solvent was removed. The residue was chromatographed on silica gel eluted with 20% EtOAc in hexane to give **14** (679 mg) quantitatively. Oil; R_f=0.42 (20% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (6H, s), 0.89 (9H, s), 1.23–1.56 (15H,m), 2.00–2.07 (2H, dt, J=7.1, 6.0 Hz), 3.59 (2H, t, J=6.5 Hz), 4.08 (2H, d, J=4.9 Hz), 5.55–5.74 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.4 (2C), 18.3, 25.7, 25.9 (3C), 29.1, 29.1, 29.3 (2C), 29.5, 32.1, 32.7, 63.2, 63.4, 128.3, 133.0; IR (neat) 3350 cm^{-1}; MS (FAB) m/z 315 (MH^+, 54). HRMS Calcd for $C_{18}H_{39}O_2Si$: MH^+, 315.2719. Found: m/z 315.2708.

(*E*)-12-(*tert*-Butyldimethylsilyl)oxy-2-dodecen-1-al (15). To a cooled solution of oxalyl chloride (0.28 mL) in CH_2Cl_2 (5 mL) at −78°C was added dropwise DMSO (0.46 mL), and the mixture was stirred for 15 min at the same temperature. A CH_2Cl_2 solution (2 mL) of alcohol **14** (680 mg, 2.16 mmol) was added slowly. After stirring for 30 min, it was quenched with Et_3N (1.5 mL) at −78°C. The mixture was slowly warmed up to 0°C for 1 h. Sat. NH_4Cl (5 mL) was added and the mixture was extracted with EtOAc (150 mL). The extract was washed with water, brine and dried over $MgSO_4$. After solvent was removed the residue was purified by column chromatography on silica gel eluting with 5% EtOAc in hexane to give **15** (556 mg) in 67% yield. Oil, R_f=0.29 (5% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (6H, s), 0.89 (9H, s), 1.30–1.53 (14H, m), 2.33 (2H, tdd, J=6.8, 6.8 and 1.6 Hz), 3.60 (2H, t, J=6.6 Hz), 6.12 (1H, ddt, J=15.6, 7.8 and 1.6 Hz), 6.85 (1H, dt, J=15.6 and 6.8 Hz), 9.50 (1H, d, J=7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.4 (3C), 18.2, 25.6, 25.9 (2C), 27.7, 29.0, 29.2, 29.2, 29.3, 32.6, 32.7, 63.1, 132.8, 158.8, 193.8; IR (neat) 1690 cm^{-1}; MS (FAB) m/z 313 (MH^+, 93). HRMS Calcd for $C_{18}H_{37}O_2Si$: MH^+, 313.2563. Found: m/z 313.2544.

(*E*)-1,1-Dibromo-13-(*tert*-butyldimethylsilyl)oxy-1,3-tridecadiene (16). To an ice cooled solution of **15** (222 mg, 0.71 mmol) and carbon tetrabromide (401 mg, 1.21 mmol) in CH_2Cl_2 (7.2 mL), was added triphenylphosphine (653 mg, 2.49 mmol) by several portions. After the addition, the reaction completed. The mixture was diluted with hexane (20 mL) and passed through short silica gel column. Fractions containing **16** was condensed and re-purified by silica gel column chromatography eluting 5% EtOAc in hexane to give **16** (293 mg) in 88% yield. Oil, R_f=0.24 (2.5% EtOAc in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (6H, s), 0.89 (9H, s), 1.24–1.53 (14H, m), 2.09 (2H, tdd, J=6.8, 6.8 and 1.3 Hz), 3.60 (2H, t, J=6.6 Hz), 5.90 (1H, dt, J=15.3 and 6.8 Hz), 6.08 (1H, ddt, J=15.3, 10.0 and 1.3 Hz), 6.89 (1H, d, J=10.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.2 (2C), 18.4, 25.8, 26.0 (3C), 28.8, 29.1, 29.4 (2C), 29.5, 32.9, 33.0, 63.3, 88.3, 127.1, 137.12, 139.6; MS (FAB) m/z 467, 469, 471 (MH^+). HRMS Calcd for $C_{19}H_{37}O_2SiBr_2$: MH^+, 467.0980, 469.0960, 471.0940. Found: m/z467.0988, 469.0970, 471.0951.

(1*Z*,3*E*)-1-Bromo-13-(*tert*-butyldimethylsilyl)oxy-1,3-tridecadiene (17). A palladium catalyst was generated at room temperature by stirring of $Pd(OAc)_2$ (5.3 mg) and triphenylphosphine (28 mg) in anhydrous benzene (2 mL) for 15 min, which was added to **16** (293 mg, 0.63 mmol) in benzene (4.3 mL). To this mixture Bu_3SnH (0.19 mL, 0.7 mmol) was added, and the mixture was stirred for 1 h at room temperature. Then, it was diluted with hexane (100 mL), and washed with water and brine. The organic layer was dried over $MgSO_4$, condensed, and chromatographed on silica gel eluting with 5% EtOAc in hexane to give **17** (207 mg) in 85% yield. Oil, R_f=0.24 (2.5% EtOAc in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (6H, s), 0.89 (9H, s), 1.23–1.57 (14H, m), 2.13 (2H, td, J=7.1 and 7.0 Hz), 3.59 (2H, t, J=6.6 Hz), 5.92 (1H, dt, J=15.0 and 7.0 Hz), 6.02 (1H, d, J=7.0 Hz), 6.36 (1H, dd, J=15.0 and 10.1 Hz), 6.58 (1H, dd, J=10.1 and 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.2 (2C), 18.4, 25.8, 26.0 (3C), 28.9, 29.2, 29.4, 29.6, 32.9, 33.0 (2C), 63.3, 105.4, 126.0, 132.8, 139.7; MS (FAB) m/z 389, 391 (MH^+). HRMS Calcd for $C_{19}H_{38}OSiBr$: MH^+, 389.1875, 391.1855. Found: m/z 389.1885, 391.1870.

(4*Z*,6*E*)-16-(*tert*-Butyldimethylsilyl)oxy-4,6-hexadecadiene (18). To an ice cooled solution of **17** (63 mg, 0.162 mmol) and $NiCl_2$(dppp) (3.6 mg, 6.6 μmol) in ether (1 mL), was added propylmagnesium bromide (0.34 mmol, 0.36 mL in 0.94 M THF solution) at room temperature. The reaction was stirred for 20 min at the same temperature, and diluted with hexane (40 mL). The mixture was washed with water, brine, dried over $MgSO_4$, and evaporated. The residual oil was purified by column chromatography on silica gel eluting with hexane to give **18** (47.8 mg) in 84% yield. Oil, R_f=0.24 (2.5% EtOAc in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (6H, s), 0.89 (9H, s), 0.92 (3H, t, J=7.3 Hz), 1.28–1.55 (16H, m), 2.08 (2H, dt, J=7.6 and 7.6 Hz), 2.14 (2H, dt, J=7.1 and 7.1 Hz), 3.59 (2H, t, J=6.6 Hz), 5.30 (1H, td, J=7.6 and 10.9 Hz), 5.65 (1H, td, J=7.1 and 15.0 Hz), 5.95 (1H, dd, J=10.9 and 10.9 Hz), 6.29 (1H, ddd, J=1.3, 10.9 and 15.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.3 (2C), 13.7, 18.4, 22.9, 25.8, 26.0 (3C), 29.2, 29.3, 29.4, 29.6, 29.7, 32.9 (3C), 63.3, 125.6, 128.8, 129.8, 134.7; MS (FAB) m/z 353 (MH^+, 25). HRMS Calcd for $C_{22}H_{45}OSi$: MH^+, 535.3240. Found: m/z 353.3242.

Bombykol. A mixture of **18** (47.8 mg, 0.136 mmol) in THF (1.5 mL) and Bu_4NF (0.14 mmol, 0.14 mL in 1 M THF solution) was stirred for 2 h at 0°C. Then, the reaction mixture was diluted with ether (60 mL) and washed with water, brine, and dried over $MgSO_4$. After solvent was evaporated, the residue was purified by column chromatography on silica gel eluted with 20% EtOAc in hexane

to give bombykol (30 mg) in 93% yield. Oil, R_f=0.40 (20% EtOAc in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (3H, t, J=7.4 Hz), 1.27–1.49 (16H, m), 2.09 (2H, dt, J=7.7 and 7.7 Hz), 2.16 (2H, dt, J=6.9 and 6.9 Hz), 3.64 (2H, t, J=6.6 Hz), 5.30 (1H, dt, J=10.9 and 7.7 Hz), 5.65 (1H, dt, J=15.2 and 6.9 Hz), 5.86 (1H, dd, J=10.9 and 10.9 Hz), 6.20 (1H, dd, J=15.2 and 10.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 22.9, 25.7 (2C), 29.2, 29.4 (2C), 29.5, 29.7, 32.8, 32.9, 63.1, 125.7, 128.8, 129.8, 134.6.

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